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Magic numbers for metallic clusters and the principle of maximum hardness

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ABSTRACT **It is shown that for relatively more stable metallic clusters (those with magic number of atoms) the chemical hardness (I–A) too is relatively larger. Thus the occurrence of magic numbers for metal clusters whose stability is determined by their electronic shell structure can be understood as a manifestation of the principle of maximum hardness. This may also represent a possible way of delineating clusters with stability dominated by their electronic shell structure from those for which the magic numbers occur as a result of their geometric structure.**

Mass spectra of clusters, both nonmetallic (1–3) and metallic (1, 2, 4, 5), show pronounced intensity for certain numbers of atoms. Points at which these intensity anomalies occur have been termed magic numbers. For nonmetallic clusters, in particular for the rare gas ones, the occurrence of magic numbers is a consequence (3, 6) of their geometric structure. For example, in the case of rare gas atoms it is argued (3, 6, 7) that clusters are formed by packing of atoms around a central atom and the most stable ones are those for which the icosahedral shells are completely filled. For metal clusters, on the other hand, magic numbers have been shown (5, 8) to be dominated by their electronic structure for up to about 1500-atom (8) clusters. Here, I show that the relative stability of these clusters is related to their chemical hardness (9). Magic numbers appear at those points where the cluster hardness has a local maximum. This is thus a manifestation of the principle of maximum hardness (10). In the following, I first discuss the energetics of metal clusters and in particular the relationship between their energies and the magic numbers. I then review the definition of hardness and the principle of maximum hardness. Finally, I calculate hardnesses for lithium clusters within the spherical jellium background model (5, 11, 12) (SJBM) with numbers of atoms in the range 2–67. I show that hardness is maximum at the magic numbers and conclude with a discussion of the results.

Energetics of Metal Clusters

Metal clusters have been studied (1, 2, 4) extensively using the spherical jellium background model. In this model the ionic charge is spread uniformly over a sphere of radius $R = r_s(NZ)^{1/3}$ where r_s is the Wigner–Seitz radius of the metal and N and Z are the number and valence, respectively, of the constituent atoms. The advantage of using this model is that the potential it gives rise to is a simple central potential so that the solution of the Schrodinger equation is greatly facilitated. The justification (4) for using this model comes from the weak pseudopotential for the alkali metals for which this model is most frequently used. Electron–electron interactions are usually accounted for by using the density-functional (13–15) approach of Kohn and coworkers (16, 17) within the local density approximation (13–15) for the exchange and correlation. For the purposes discussed here, however, the local density approximation is not applicable—neither for atomic (18–20) nor for *all* the cluster (refs. 21 and 22; unpublished work) anions does it lead to convergent solutions. The reason for the failure of this approximation is well understood (24–26) to be the effect of self-interaction in the exchange in this approximation. For my calculations I use a formalism proposed by Harbola and Sahni (27, 28). In this formalism, the exchange potential is self-interaction free and leads to energies, both for neutral atoms (29, 30) and for atomic anions (31), that are essentially the same as the Hartree–Fock energies. I perform the calculations within the exchange-only approximation (32) of the density-functional approach. For the purpose of demonstrating the principle of maximum hardness, correlation effects are insignificant (unpublished work; details on these calculations can be obtained from M.K.H.).

Stability of metal clusters is studied (4, 5) by plotting the second energy difference

$$\Delta_2(N_A) = E(N_A + 1) + E(N_A - 1) - 2E(N_A) \qquad [1]$$

against the number N_A of atoms in the cluster. As is well known, $\Delta_2(N_A)$ is the relative binding energy of a cluster with N_A atoms with respect to those with $N_A + 1$ and $N_A - 1$ atoms, and therefore peaks in it represent relatively more stable clusters. This quantity is plotted in Fig. 1. It is clear from Fig. 1 that $\Delta_2(N_A)$ is close to zero except for $N_A = 2$, 8, 18, 20, 34, 40, and 58. The peaks at these numbers correspond to the intensity anomalies or magic numbers of the mass spectrum at $N_A = 2$, 8, 20, 34, 40, and 58. A weak peak at $N_A = 18$ is also observed (5) in the spectrum. Thus it is clear that the peaks in the plot for $\Delta_2(N_A)$ delineate the abundance of magic number clusters. Since the energy is dominated by its electronic part, the magic numbers are presumably attributed to electronic shell structure effects. However, so far as I know, no detailed electronic explanation has heretofore been given.

Hardness and the Principle of Maximum Hardness

The chemical hardness η of a species is defined (9) by density-functional theory to be the second derivative of the ground-state energy E with respect to the number of electrons N at constant external potential $v(\mathbf{r})$:

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\mathbf{r})} \qquad [2a]$$

$$= \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{v(\mathbf{r})}, \qquad [2b]$$

where μ is the chemical potential (33) of the system

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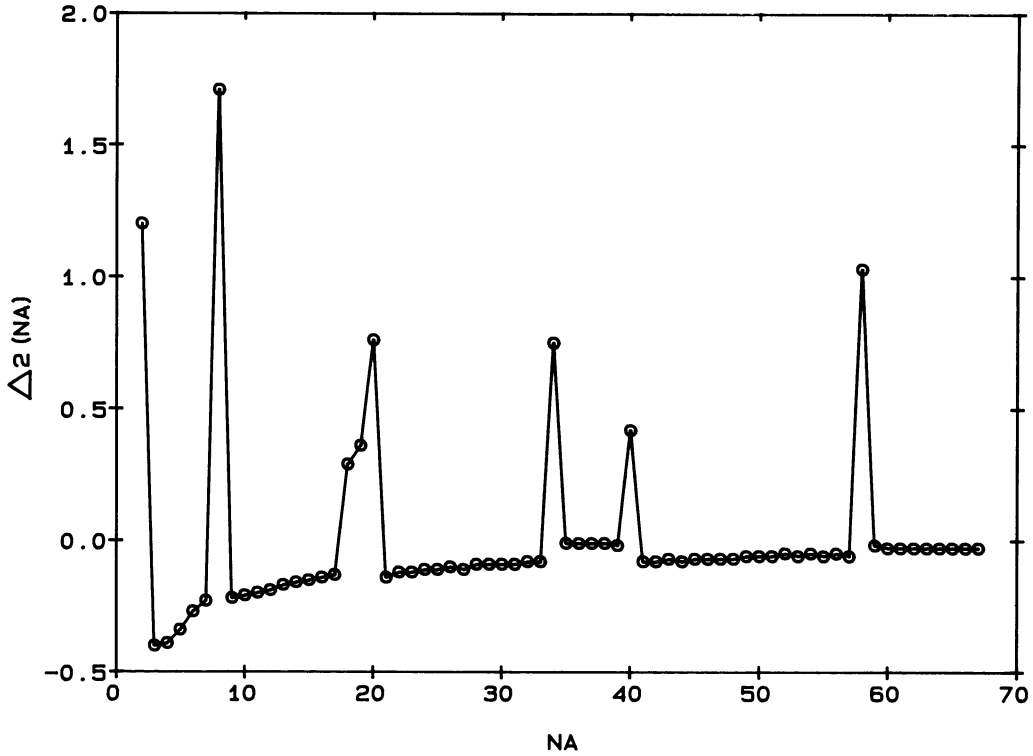

FIG. 1. Second energy difference $[\Delta_2(N_A)]$ for lithium clusters versus number of atoms (N_A).

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{v(\mathbf{r})} \quad [3a]$$

$$= \frac{\delta E_v[\rho]}{\delta \rho(\mathbf{r})}, \quad [3b]$$

where $\rho(\mathbf{r})$ is the electronic density. Eq. **3b** follows from the Hohenberg–Kohn theorem (13–16). The factor of 1/2 in Eq. **2** is arbitrary. Since the E versus N curve is not smooth but piecewise linear (34), neither μ nor η can be evaluated exactly. They are defined using the finite-difference approximation as

$$\mu = -\frac{I + A}{2} \quad [4]$$

and

$$\eta = \frac{I - A}{2}, \quad [5]$$

where I and A are the ionization potential and electron affinity, respectively, of the system. Inverse of hardness is defined (35) to be the softness and is

$$S = \frac{1}{2\eta} \quad [6a]$$

$$= \left(\frac{\partial N}{\partial \mu}\right)_{v(\mathbf{r})}. \quad [6b]$$

With these definitions of the chemical potential, hardness, and softness, the HSAB principle (36) has been rationalized (9, 37).

Another principle associated with the concept of hardness is the principle of maximum hardness (10), which states ". . .molecules arrange themselves so as to be as hard as possible." Thus, according to this principle, the larger the value of I–A, the more stable a molecule or a cluster would be. This has been formally derived (38) using fluctuation formulas (35) for softness. A plausibility argument for this principle can be given as follows. It is well known (9) that the exchange of electrons between different species is governed by the chemical potential. However due to the piecewise continuous nature (34) of the E versus N curve, the chemical potential for a species is not a unique number but has a range of $-I$ to $-A$ (39). Thus, a system in contact with a reservoir with chemical potential in this range would tend not to exchange electrons with the reservoir. But this range of the chemical potential is nothing but hardness as defined in Eq. **5**. Thus, given a number of systems all with the same average chemical potential as defined by Eq. **4**, larger hardness for a system implies that a relatively larger number of channels will not be available for it to exchange electrons with.

Hardness for Metal Clusters

In Fig. 2, I plot (I–A), which is two times the hardness, for lithium clusters with numbers of atoms in the range of 2–67 versus the number of atoms. As shown, hardness decreases as the number of atoms increases. How I–A changes with the size of the cluster is discussed below. The principal interest here lies in the fact that at N_A = 2, 8, 18, 20, 34, 40, and 58, hardness deviates from an otherwise smooth curve, showing distinct peaks for these clusters. These peaks are at precisely the same points (see Fig. 1) where the intensity anomalies occur. Thus, peaks in the hardness plot also delineate the abundance of magic number clusters. Equivalently, for relatively more stable clusters, the hardness shows a local maximum. This is the principle of maximum hardness.

How the hardness for metallic clusters changes with their size can be seen from the size dependence of the ionization potential and electron affinity of these systems. For metal clusters I and A are (ref. 40; unpublished work) on the

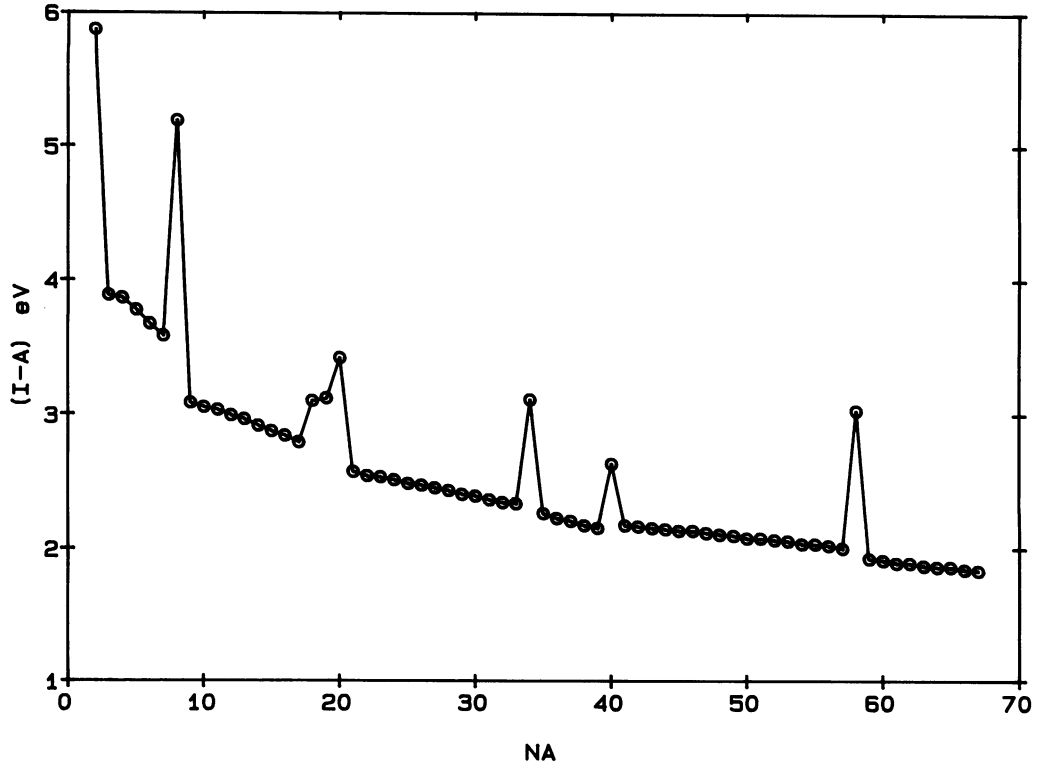

FIG. 2. Chemical hardness (I–A) versus number of atoms (N_A) for lithium clusters.

average (there are oscillations due to the shell structure that are being ignored)

$$I = W + \frac{1}{2}\frac{1}{(R+a)} \quad \text{hartrees} \qquad [7a]$$

and

$$A = W - \frac{1}{2}\frac{1}{(R+a)} \quad \text{hartrees,} \qquad [7b]$$

where W is the work function for the bulk metal, R is the radius of the cluster, and a is a microscopic distance that accounts for the fact that electrons in the jellium sphere are not confined to radius R but are spread out (1 hartree = $4\pi^2me^4/h^2 \approx 27.21$ eV = 4.360 aJ). There are other forms (41, 42) of Eq. 7 that use 3/8 in place of 1/2 in Eq. **7a** and 5/8 in Eq. **5b**. Eq. 7 is derived by assuming that the chemical potential of a cluster does not change as its size increases. In recent work (43, 44) some conclusions of ref. 40 have been revised. In any case hardness for a cluster of radius R is given as

$$\eta = I - A = \frac{1}{(R+a)} \quad \text{hartrees.} \qquad [8]$$

The factor of 1/2 has been dropped here for convenience. It has been confirmed that I–A or hardness indeed goes as given by Eq. **8**. What remains more interesting, however, is that at magic numbers it shows sharp maxima in accord with the principle of maximum hardness.

Discussion

I have demonstrated above that for magic number metallic clusters, which are the most abundant ones in the mass spectrum, the corresponding hardness is also a maximum. This may represent a possible way of determining whether the stability of clusters with number of atoms in a certain range is dominated by their electronic or by their geometric structure. For clusters for which magic numbers are results of their geometric structure, the chemical hardness (I–A) may not show such marked structure as it does for those that display magic numbers due to their electronic shell structure. Thus, the difference in the behavior of (I–A) may delineate the two kinds of clusters.

The demonstration of the principle of maximum hardness here agrees well with the original statement (10) of the principle of maximum hardness. Recent proof (38) of the principle, however, has been provided under the condition that the external potential remain a constant. For the case of clusters that I have considered here, as well as in various other examples (23, 45), the external potential is not a constant and changes with the number of electrons. The chemical potential for all the clusters on the other hand is on the average a constant equal to W. Does this mean that the proof provided (38) is a corollary of a more general proof? The answer is not clear. What is clear however is that hardness plays a fundamental role in determining the stability of diverse systems.

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